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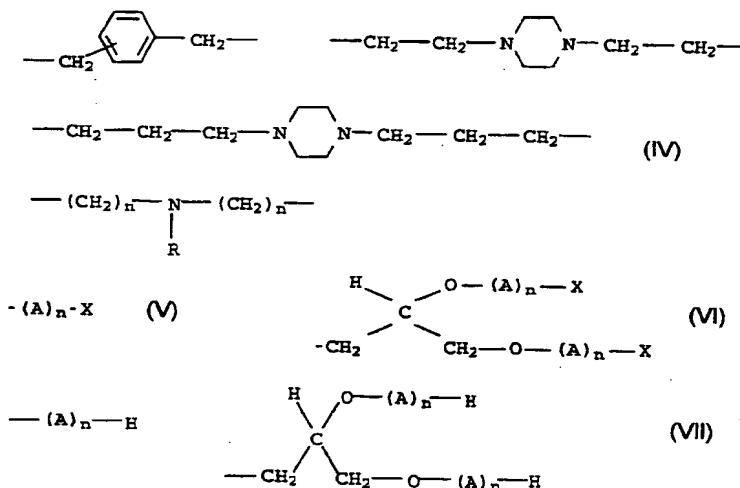
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(54) Title: ZWITTERIONIC POLYAMINES AND A PROCESS FOR THEIR PRODUCTION



(57) Abstract: A zwitterionic polyamine comprising a linear or branched hydrophobic polyamine backbone having 2 to 10 tertiary amino nitrogen atoms and a spacer between two tertiary nitrogen atoms wherein the spacer is, for example selected from C₈-C₁₆-alkylene, C₅-C₁₅-cyloalkylene, wherein in formula (IV) R = C₁- to C₂₂-alkyl or C₇-C₂₂-aralkyl and n = 3 to 6, at least one tertiary amine end group of the polyamine backbone contains two groups having formula (V) or (VI), wherein A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit, n is a number of from 1 to 50, X is an anionic group such as -SO₃M, with the proviso that in formula (VI) one X may also be hydrogen and M is hydrogen, alkali metal or ammonium, or contains one group of formula (V) or (VI) and one group selected from radicals consisting of formula (VII), C₁- to C₂₂-alkyl and C₇-C₂₂-aralkyl, the meaning of A and n is the same as in formula (V) or (VI), said zwitterionic polyetherpolyamine having a molecular weight up to 9000 and optionally containing up to 100 % of the nitrogen atoms quaternized, and a process for the production of zwitterionic polyamines by alkoxylating said polyamines, introducing anionic groups into the alkoxylated polyamines and optionally quaternizing them before or after the introduction of anionic groups. The zwitterionic polyamines are used in detergents.

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Zwitterionic polyamines and a process for their production

Description

5

The present invention relates to zwitterionic polyamines and a process for their production by alkoxylation of polyamines and introduction of anionic groups.

10 Background of the invention

EP-A-0,111,976 relates to watersoluble zwitterionic compounds having clay soil removal/anti-redeposition properties. An example of such a compound is a with chlorosulfonic acid sulfated quaternized addition product of ethoxylated tetraethylenepentamine with a total degree of ethoxylation of 21.

EP-A-0,112,592 relates to zwitterionic polymers which are for example obtained by alkoxylation of polyalkyleneamines such as triethylenetetramine or tetraethylenepentamine or of polyethylenimine, sulfonation of the alkoxyated products and subsequent quaternization. The zwitterionic products disclosed in the above patents have clay-soil removal and anti-redeposition properties when used in detergent compositions, however their effectiveness in dispersing and removing clay embedded in the fabric into the laundry liquor is not sufficient. Furthermore the specifically disclosed compounds of this literature reference are thermally instable.

GB-A-2,220,215 relates to sulfated alkoxyated mono- or polyamines derived from polymethylenediamines with 2 - 6 methylene groups between the nitrogen atoms or polyalkylenepolyamines in which the alkylene contains 2-4 carbon atoms and containing 3-6 amino groups. They may bear a long chain-alkyl substituent at one of the nitrogen atoms and are quaternized. However it was found that these polymers are not favorable for clay soil removal within laundry operations where anionic surfactants are present.

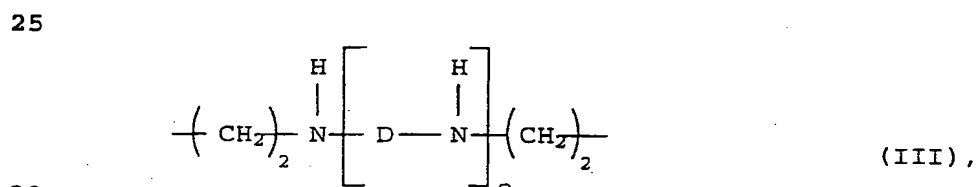
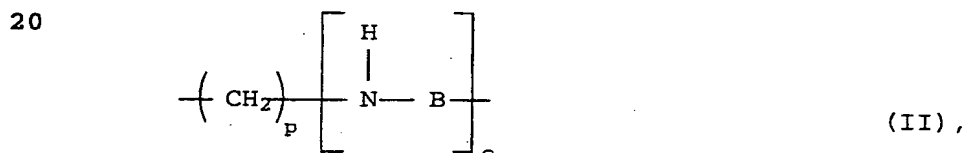
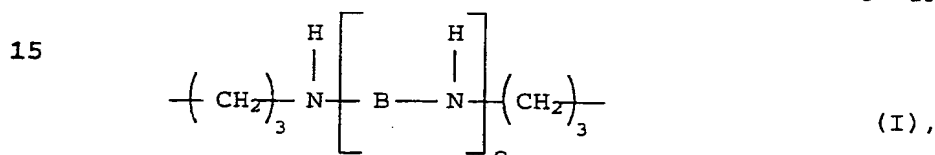
U.S. Patent 4,739,094 discloses alkoxyated aminopolyethers containing units of ethylene oxide and propylene oxide and having a molecular weight of from 10,000 to 150,000. The alkoxyated aminopolyethers are water-soluble and are used in 5 to 60 % strength by weight aqueous solution in the preparation of coal/water slurries. If appropriate, the alkoxyated aminopolyethers can also be reacted with carboxylic acid anhydrides, amidosulfonic acids and urea, acid chlorides of sulfur or of phosphorus or

chloroacetic acid esters. The reaction products can be converted into ionic compounds by subsequent neutralization or hydrolysis.

It is therefore an object of the invention to provide new polymers with improved thermal stability.

Summary of the invention

The above object is achieved with a zwitterionic polyamine comprising a linear or branched hydrophobic polyamine backbone having 2 to 10 tertiary amino nitrogen atoms and a spacer between two tertiary amino nitrogen atoms wherein the spacer is selected from the group consisting of C₃-C₁₅-alkylene, C₅-C₁₅-cycloalkylene



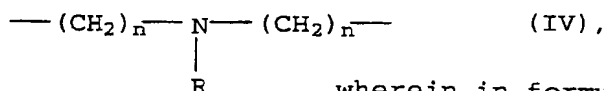
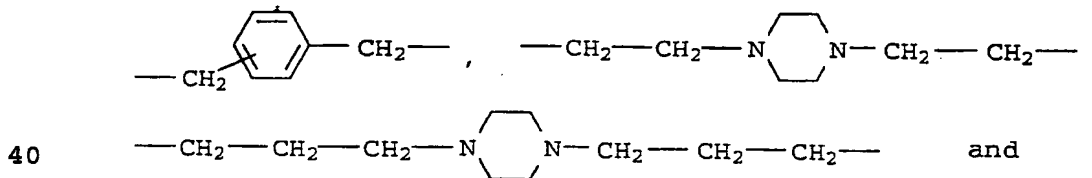
wherein in formula I, II and III

B is C₂-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

D is C₄-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

O is 1 or 2,

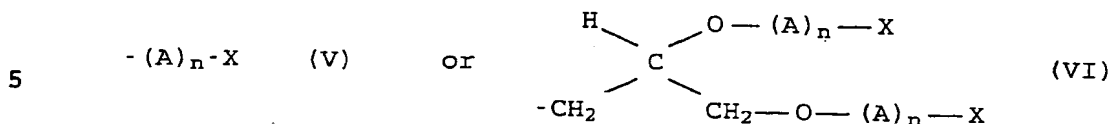
p is 3 to 8



wherein in formula IV

R = C₁- to C₂₂-alkyl or C₇-C₂₂-aralkyl
and n = 3 to 6,

at least one tertiary amine end group of the polyamine backbone contains two groups having the formula



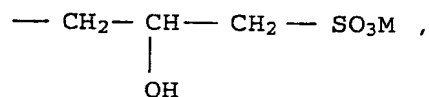
wherein

A means an ethylene oxide unit, a propylene oxide unit, a unit of
 10 butylene oxides and a tetrahydrofuran unit,

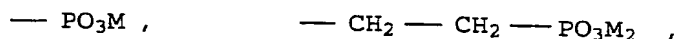
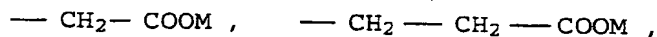
n is a number of from 1 to 50,

X is $\text{—SO}_3\text{M}$, $\text{—CH}_2\text{—CH}_2\text{—SO}_3\text{M}$, $\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—SO}_3\text{M}$,

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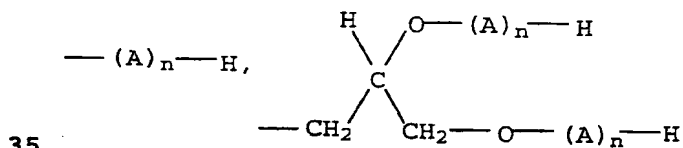
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with the proviso that in formula VI one X may also be hydrogen
 25 and

M is hydrogen, alkali metal or ammonium,

or contains one group of formula V or VI and one group selected
 30 from radicals consisting of



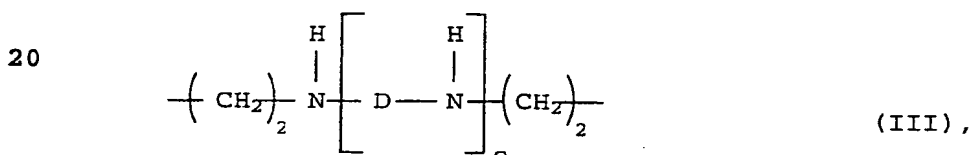
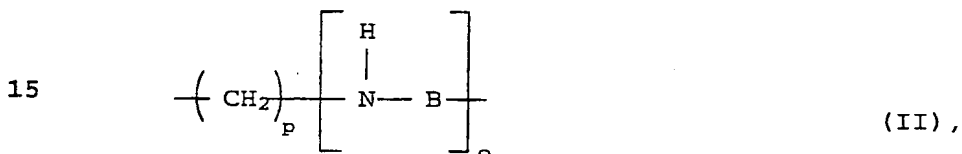
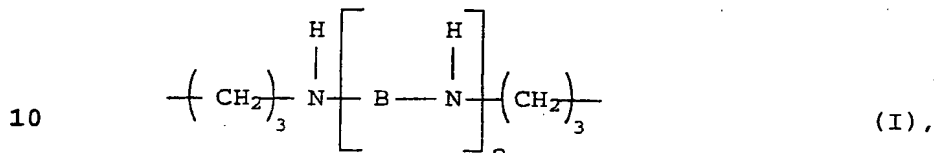
C₁- to C₂₂-alkyl and C₇-C₂₂-aralkyl, the meaning of A and n is the same as in formula V or VI,

40 said zwitterionic polyamine having a molecular weight up to 9,000 optionally containing up to 100% of the nitrogen atoms quaternized.

The object is also achieved with a process for the production of
 45 a zwitterionic polyamine which comprises a first step wherein

- (i) a linear or branched hydrophobic polyamine having 2 to 10 tertiary amino nitrogen atoms and a spacer between two tertiary amino nitrogen atoms wherein the spacer is selected from the group consisting of

C₈- to C₁₆-alkylene, C₅- to C₁₅-cycloalkylene



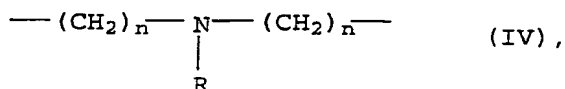
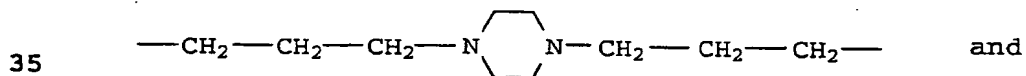
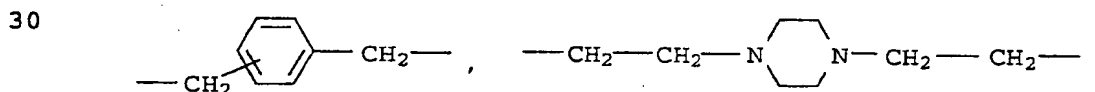
wherein in formula I, II and III

B is C₂-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

D is C₄-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

o is 1 or 2,

p is 3 to 8



wherein in

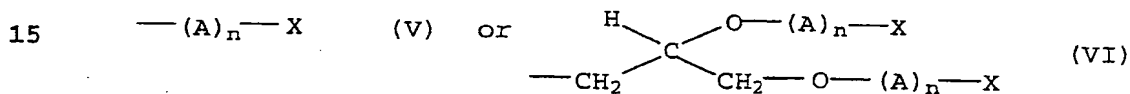
in formula IV R = C₁- to C₂₂-alkyl or C₇-C₂₂-aralkyl and
n = 2 to 6,

is reacted with

5

(ii) at least one C₂- to C₄-alkylene oxide or tetrahydro furane at such a ratio that on each NH group of the polyamine 1 to 50 units of the alkylene oxide or of tetrahydrofuran are added,

5 a second step wherein the alkoxyated polyamine obtained in the first step is reacted with a compound selected from the group consisting of a halogen sulfonic acid, halogen phosphorous acid, vinyl sulfonic acid, propane sultone, halogen acetic acid, acrylic acid, methacrylic acid, vinyl phosphorous
10 acid and the alkali metal or ammonium salts of the said acids, in such a manner that at least one tertiary amine end group of the alkoxyated polyamine contains two groups having the formula

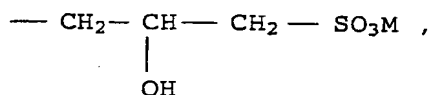


wherein

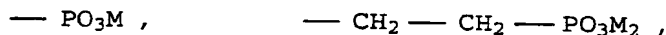
20 A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit,

n is a number of from 1 to 50,

25 X is $\text{---SO}_3\text{M}$, $\text{---CH}_2\text{---CH}_2\text{---SO}_3\text{M}$, $\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---SO}_3\text{M}$,



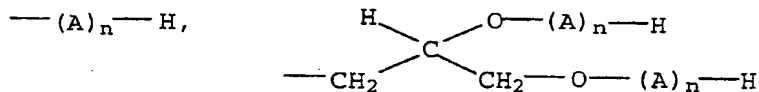
30 $\text{---CH}_2\text{---COOM}$, $\text{---CH}_2\text{---CH}_2\text{---COOM}$,



35 with the proviso that in formula VI one X may also be hydrogen and

M is hydrogen, alkali metal or ammonium,

40 or contains one group of formula V or VI and one group selected from radicals consisting of



the meaning of A and n is the same as in formula V or VI,

and optionally

- 5 a third step wherein up to 100% of the tertiary nitrogen atoms of the reaction product obtained in the second step are quaternized, said degree of quaternization, may also be obtained by first quaternizing the reaction product obtained in the first step and subsequently carrying out the second step.

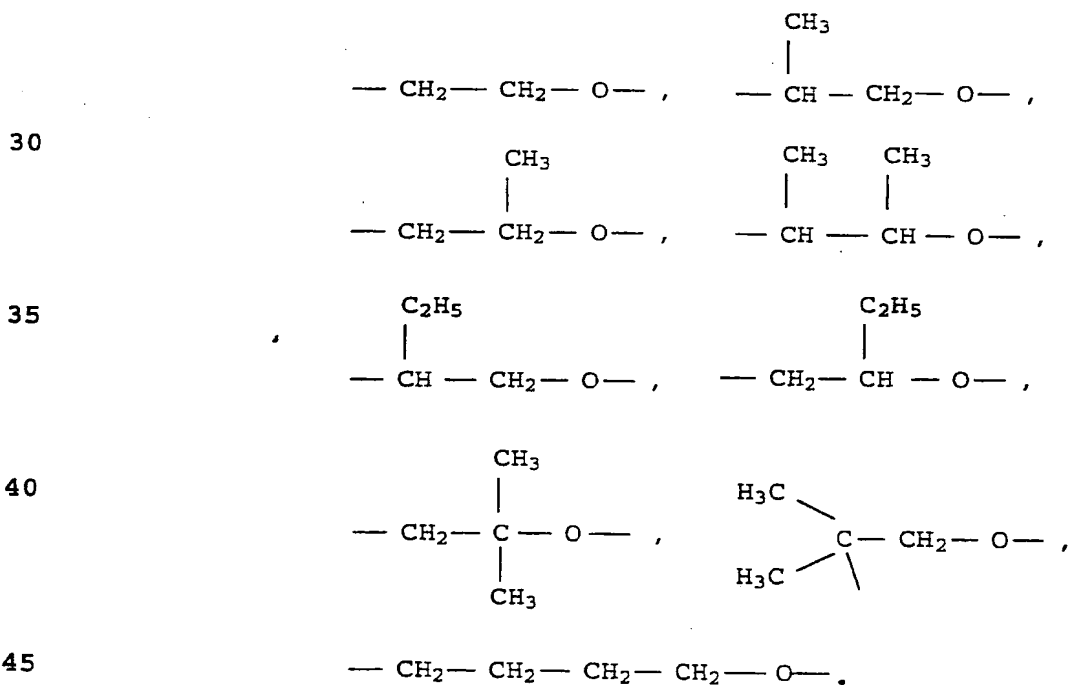
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Preferred zwitterionic polyamines contain two groups of formula V or VI attached to the tertiary nitrogen atoms of the end groups of the polyamines. Especially preferred zwitterionic polyamines contain the nitrogen atoms of the end groups of the polyamine

- 15 backbone quaternized and, as substituents, two groups of formula V or VI and one C1- to C22- alkyl group or a hydroxyalkyl group. In most cases the nitrogen end groups of the polyamine backbone are quaternized and contain as substituents two groups of formula V and a C1- to C22- alkyl group. Other preferred zwitterionic
- 20 polyamines contain quaternized amino nitrogen end groups bearing, as substituents, two groups of formula V and a hydroxyethyl or hydroxypropyl group.

The substituent A in formulae V and VI may have the following

25 structures:



Other zwitterionic polyamines are characterized in that the spacer between two nitrogen atoms of the polyamine backbone is a cyclic C5- to C15-alkylene group.

- 5 Of particular interest are zwitterionic polyamines wherein the polyamine backbone between the nitrogen atoms is derived from an amine selected from the group consisting of bis(hexamethylene)triamine, N,N'-bis(3-aminopropyl)piperazine, N,N'-bis(2-aminoethyl)piperazine and bis(3-aminopropyl)hexamethylenediamine and
 10 wherein at least one tertiary amine end group of the polyamine backbone contains two groups having formula V or VI.

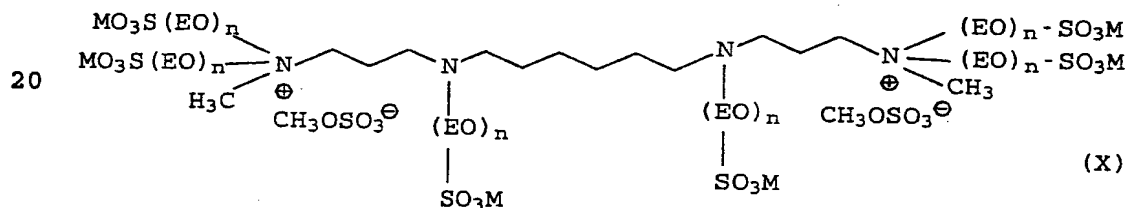
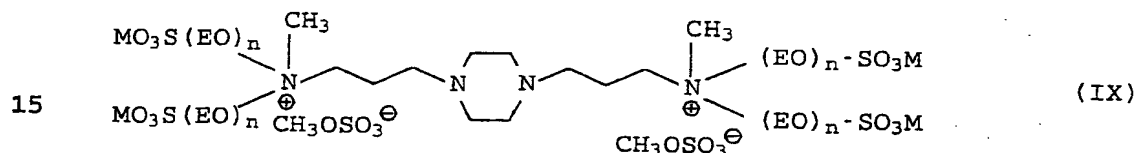
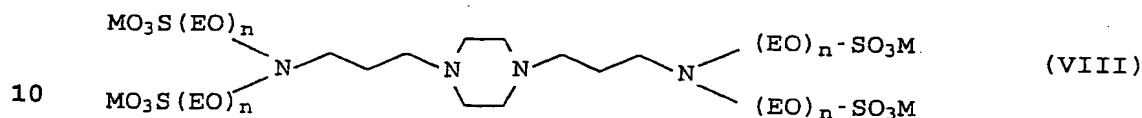
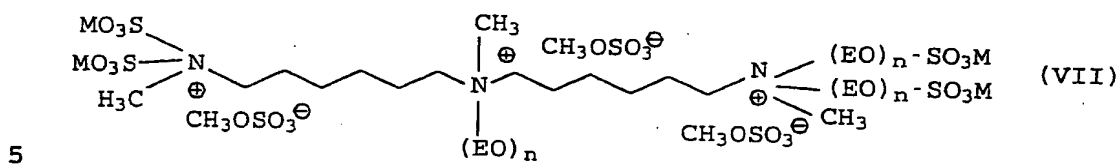
The zwitterionic polyamine is derived from a linear or branched hydrophobic polyamine. The backbone of the polyamine contains 2
 15 to 10 tertiary amino nitrogen atoms and has one spacer between two tertiary amino nitrogen atoms. Polyamines containing a C₈- to C₁₆-alkylene group as spacer are for example 1,8-diaminooctane, 1,10-diaminodecane and 1,12-diaminododecane. Examples of suitable polyamines containing the above spacers of formula I - IV are di-
 20 propylenetriamine, tripropylenetetramine, bis(hexamethylene)triamine, bis(octamethylene)triamine, aminoethylpropylenediamine, aminoethylbutylenediamine, aminoethylhexamethylenediamine, N,N'-bis(aminoethyl)propylenediamine, N,N'-bis(aminoethyl)butylenediamine, N,N'-bis(aminoethyl)hexamethylenediamine, N,N'-bis(amino-
 25 propyl)ethylenediamine, N,N'-bis(aminopropyl)butylenediamine, N,N'-bis(aminopropyl)hexamethylenediamine, N,N'-bis(aminopropyl)ethylenediamine, N,N-bis(3-aminopropyl)-N-methylamine, N-(dimethylaminopropyl)propylenediamine, N,N'-dimethyl-1,3-diaminopropane, N,N-
 30 bis(3-aminopropyl)-N-octylamine and N,N-bis(3-aminopropyl)-N-ethylamine.

Polyamines with spacers consisting of a cyclic C5- to C15-alkylene group are for example 1,3-cyclohexylenediamine,
 35 4-methyl-1,3-cyclohexylenediamine, 2-methyl-1,3-cyclohexylenediamine, isophoronediamine and 4,4'-diamino(biscyclohexylene)methane.

The zwitterionic polyamines can also be prepared from polyamines
 40 which contain other cyclic spacers. Such polyamines are, for example, o-, m-, and p-di(aminomethylen)benzene, N,N'-bis(aminoethyl)piperazine, N,N'-bis(aminopropyl)piperazine and N-aminopropylpiperazine.

- 45 Especially preferred zwitterionic polyamines may be characterized by the following formula

8



25 wherein

EO is $-\text{CH}_2-\text{CH}_2-\text{O}-$

M is H, Na, K or ammonium and

n is 15-25.

30

The weight average molecular weight Mw of the zwitterionic poly-polyamines is up to 9,000, preferably of from 1,500 to 7,500 and more preferably of from 2,000 to 6,000. The zwitterionic poly-amines can be soluble or dispersible in water and aqueous or non-
 35 aqueous solvents or formulations. In one preferred embodiment of the present invention they are water-soluble. These water soluble zwitterionic polyetherpolyamines are used in laundry detergent compositions and have an excellent degree of clay soil removal from fabrics.

40

The zwitterionic polyamines are net anionic. Preferably the average number of anionic charges resulting from groups X in formulae V and VI exceeds the average number of cationic charges resulting from protonated or quaternized amine groups by a factor of more
 45 than 1.2, more preferred of more than 1.5, most preferred of more than 1.8.

The zwitterionic polyamines of the invention are prepared in a multistage process. In the first step of this process a linear or branched polyamine having 2 to 10 primary or secondary nitrogen atoms and containing one of the above spacers between two nitrogen atoms is reacted with at least one C₂- to C₄-alkylene oxide or tetrahydrofuran at such a ratio that on each NH group of the polyamine 1 to 50, preferably 15 to 25 alkylene oxide units or tetrahydrofuran units are added. Ethylene oxide and propylene oxide are the preferred alkoxyating agents. If a mixture of alkylene oxides is added to the amino nitrogen then the polymerized alkylene oxides may be present in statistical distribution or as blocks. For example one can add first 10 to 20 of ethylene oxide units per NH group in the polyamine and then add 5 to 10 propylene oxide units or vice versa.

Most preferred ethylene oxide alone or combinations of 1-15% propylene oxide or 1-10% butylene oxide with 85-99, 90-99% ethylene oxide respectively are used. If a combination of ethylene oxide and propylene oxide or butylene oxide is used preferably the propylene oxide or butylene oxide is reacted first with the NH groups of the polyamine and the ethylene oxide is added after that.

The above described procedure gives polyalkoxylated products which have groups of formula

- (A)_n -H , wherein A and n have the meaning given for formula V.

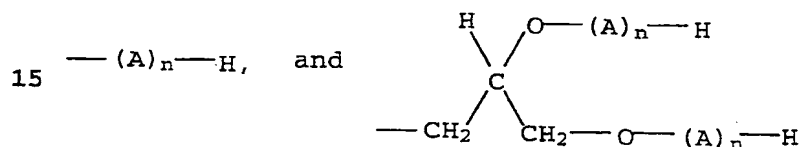
The linear or branched polyamines are preferably ethoxylated in the first step of the production of the zwitterionic polyamines.

In order to produce zwitterionic polyamines having end groups of formula VI a linear or branched polyamine having 2 to 10 nitrogen atoms and containing at least 2 primary or secondary amino nitrogen groups is reacted with up to 1 glycidol per NH group. The reaction product thus obtained is in the first step of the process according to the invention alkoxyated at the OH groups and remaining NH groups as described above. The reaction of glycidol with said polyamine may be carried out to such an extent that at least 50 to 100% of the NH groups of the polyamine are substituted by one glycidol unit.

In the second step of the production of the zwitterionic polyamines an anionic group is introduced into the alkoxyated polyamines obtained in the first step. This may be achieved by reacting the alkoxyated polyamines in a Michael type addition reaction with acrylic acid, methacrylic acid, vinyl sulfonic

acid, vinylphosphonic acid or their alkalimetal or ammonium salts or by reacting them with halogen sulfonic acid, halogen phosphorous acid, propane sultone or halogen acetic acid. The preferred component for introducing anionic groups is chlorosulfonic acid.

5 Dependent on the amount of anionic agent used in the second step zwitterionic products are obtained which contain either two substituents of formula V or VI or contain only one of them, if, for instance, only one mole of the anionic agent is used per one mole
10 of OH end group of the alkoxyated polyamine. The non-reacted end groups of the alkoxyated polyamine may be characterized by a group selected from radicals consisting of



the meaning of A and n is the same as in formula V or VI.

20 The degree of substitution of the OH groups in the alkoxyated polyamines is such, that the finally resulting zwitterionic polyamine is net anionic at the pH of intended use; e.g. from 40% up to 100% of the OH group are substituted by an anionic group. Preferably more than 60%, more preferred more than 80%, most preferred
25 90-100% of the OH-groups are substituted by an anionic group.

Moreover the zwitterionic polyamines may also contain only one substituent of formula V or VI and instead of the above described
30 radicals a C₁- C₂₂-alkyl group or a C₇- to C₂₂-aralkyl group. Such compounds result when the polyamine used in the first step contains secondary amino groups having a C₁- to C₂₂-alkyl or a C₇- to C₂₂-aralkyl substituent.

35 The zwitterionic polyamines obtained in the second step may optionally reacted in a third step with a quaternizing agent. Alternatively, quaternized products may also be obtained by first quaternizing the reaction products obtained in the first step, i.e. the polyalkoxyated polyamines. Suitable quaternization
40 agents are for example C₁- to C₂₂-alkylhalides, C₇- to C₂₂-aralkyl halides C₁-C₂-dialkylsulfates or alkylene oxides. Examples of quaternizing agents are dimethyl sulfate, diethyl sulfate, methyl chloride, ethyl chloride, methyl bromide, ethyl bromide, butyl bromide, hexyl chloride, benzyl chloride, benzyl bromide,
45 ethylene oxide or propylene oxide. Dialkylsulfates, C₁-C₄-alkylchlorides and benzyl chloride are preferred. Dimethyl sulfate is the most preferred quaternizing agent. Up to 100% of the tertiary

nitrogen atoms of the zwitterionic polyamine may be quaternized. If there is a quaternization step, then the degree of quaternization is, for example, 10 to 100%, preferably at least 25 % and more preferably 75 to 100%.

5

According to a preferred embodiment of the process for the production of zwitterionic polyamines in the first step

(i) a polyamine selected from the group consisting of
10 bis(hexamethylene)triamine, bis(aminopropyl)piperazine,
N,N'-bis(aminopropyl)hexamethylenediamine and
N,N,N',N'',N''-penta(2,3-dihydroxypropyl)-bis(hexamethylene)triamine - the latter is obtained by reacting
15 bis(hexamethylene)triamine with glycidol in a molar ratio
of 1:5) - is reacted with

(ii) an alkylene oxide selected from the group consisting of
ethylene oxide, propylene oxide, butylene oxide and mix-
tures of the said alkylene oxides, at such a ratio that
20 on each NH group of the polyamine 15 to 40 units of the
alkylene oxide are added,

in the second step

the alkoxyated polyamine obtained in the first step is reacted
25 with chlorosulfonic acid in such ratio that at least one tertiary
end group of the polyamine contains two groups having the formula



30 A is an ethylene oxide unit, a propylene oxide unit or a
butylene oxide unit,
n is 15 - 40 and
X is SO₃H,

35 and

in the third step

the zwitterionic reaction product of the second step is quater-
nized with dimethyl sulfate, methyl chloride or benzyl chloride.

40 The quaternization can also be carried out as a second step in
the multistage process for the production of zwitterionic poly-
amines. The alkoxyated polyamine obtained in the first step is
quaternized up to 100 % and subsequently reacted with chlorosul-
fonic acid or another agent capable to introduce an anionic
45 group. This procedure is preferred for the production of quater-
nized zwitterionic polyamines.

The zwitterionic polyamines are used as additive in laundry detergent compositions which provide enhanced hydrophilic soil, inter alia, clay, removal benefits. The new zwitterionic polyamines are especially useful in detergents comprising a surfactant system which comprises mid-chain branched surfactants inter alia mid-chain branched alkyl sulphonates. The zwitterionic polyamines are additionally used as effective dispersants for hydrophilic particles within aqueous and nonaqueous solutions and formulations.

10

The degree of quaternization and of sulfatation was determined by ^1H -NMR. The amine number was determined by amine titration according to DIN 16 945.

15 Example 1

(a) Ethoxylation of bis(hexamethylene)triamine ("BHMT")

A pressurizable 5 l autoclave fitted with a stirrer and a heating device was sealed and three times pressurized with nitrogen at 10 bar. 150.5 g (0.7 mole) of BHMT and 15 g of water were placed in the autoclave which was heated to 80°C. The autoclave was then sealed pressure-tight and three times pressurized with nitrogen at 5 bar and thereafter the pressure released. The contents of the autoclave were heated while stirring to 110°C. At this temperature 157.1 g (3.57 moles) of ethylene oxide were added continuously while maintaining the temperature between 110 - 120°C and the maximum pressure up to 5 bar. The reaction mixture was stirred until the pressure was constant and then cooled to about 80°C. The pressure was then released, the autoclave three times pressurized with nitrogen at 5 bar and 9.2 g of a 50% strength by weight sodium hydroxide solution were added.

The autoclave was then sealed and vacuum continuously applied to remove the water. The contents of the reactor were heated for four hours at 120°C and at a pressure of 10 mbar. Vacuum was removed with nitrogen and the autoclave heated to 140°C. Between 140 and 150°C 2,926 g (66.5 moles) of ethylene oxide were continuously introduced into the autoclave while stirring. The maximum pressure was 10 bar. The reaction mixture was stirred until the pressure was constant. The contents of the reactor were then cooled to 80°C and the reactor three times pressurized with nitrogen at 5 bar. 3,238 g of a reaction product was obtained which was an ethoxylated BHMT

containig 20 ethylene oxide units per NH group of bis(hexa-methylene)triamine ("BHMT EO20").

- (b) Quaternization of ethoxylated bis(hexamethylene)triamine with
5 20 moles of ethylene oxide per NH group in BHMT

10 Into a weighed, 2000ml, 3 neck round bottom flask fitted with argon inlet, condenser, addition funnel, thermometer, mecha-nical stirring and argon outlet (connected to a bubbler) is added 455.0 g of BHMT EO20 (0.295mol N, 98% active, M_w 4,626 g/mole) and methylene chloride (1000g) under argon. The mixture is stirred at room temperature until the polymer has dissolved. The mixture is then cooled to 5°C using an ice
15 bath. Dimethyl sulfate (39.5g, 0.31mol, 99%, m.w.-126.13) is slowly added using an addition funnel over a period of 15 minutes. The ice bath is removed and the reaction is allowed to rise to room temperature. After 48 hrs. the reaction is complete. The obtained product was analyzed by titration of the amine-number and by ^1H -NMR integration to have more then 90%
20 of the nitrogen atoms quaternized.

- (c) Sulfation of quaternized ethoxylated bis(hexamethylene)tri-amine

25 Under argon, the reaction mixture from the quaternization step (b) is cooled to 5°C using an ice bath (0.59 mol OH). Chlorosulfonic acid (72g, 0.61 mol, 99%, mw-116.52) is slowly added using an addition funnel. The temperature of the reaction mixture is not allowed to rise above 10°C. The ice
30 bath is removed and the reaction is allowed to rise to room temperature. After 6 hrs. the reaction is complete. The reaction is again cooled to 5°C and sodium methoxide (264g, 1.22 mol, Aldrich, 25% in methanol, m.w.-54.02) is slowly ad-ded to the rapidly stirred mixture. The temperature of the
35 reaction mixture is not allowed to rise above 10°C. The reaction mixture is transferred to a single neck round bottom flask. Purified water (1300ml) is added to the reaction mix-ture and the methylene chloride, methanol and some water is stripped off on a rotary evaporator at 50°C. The clear, light
40 yellow solution is transferred to a bottle for storage. The final product pH is checked and adjusted to ~9 using 1N NaOH or 1N HCl as needed. The obtained product was analyzed by ^1H -NMR integration to have more then 90% of the OH-end groups of the polyethylene oxide chains sulfated.

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Examples 2 - 5

According to the procedure given in Example 1 (a) the following amines

5

Amine 1: bis(hexamethylene) triamine

Amine 2: bis(aminopropyl) piperazine

Amine 3: N,N'-bis(aminopropyl) hexamethylenediamine

10 Amine 4: N,N,N',N'',N''-penta(2,3-dihydroxypropyl)-bis(hexa-
methylenetriamine which is the reaction product of 1
mole of bis(hexamethylene) triamine with 5 moles of glyci-
dol

were reacted with ethylene oxide in the amounts given in Table 1.

15 The ethoxylated amines were then - with the exception of Example
5 - quaternized following the procedure given in Example 1 (b)
and subsequently sulfated according to the procedure of Example 1
(c). The amounts of dimethylsulfate and chlorsulfonic acid were
adjusted appropriately. The degree of quaternization and sulfa-
20 tion is given in Table 1.

Table 1

25	Example	Amine No.	Moles of EO* added per mole of NH groups in amine	Amine number of EO addi- tion product	% quaterni- zation	% sulfa- tion
	2	1	20	40.6	90	50
	3	2	20	62.3	90	90
30	4	3	20	29.9	90	90
	5	4	10	29.2	0	90

* EO: ethylene oxide

35

40

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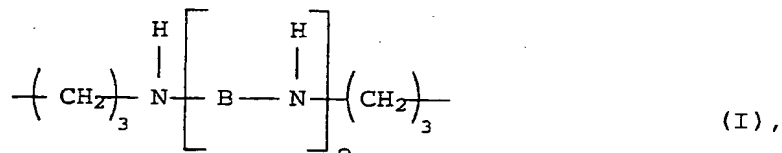
Zwitterionic polyamines and a process for their production

Claims

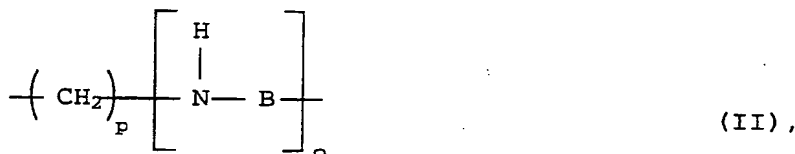
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1. A zwitterionic polyamine comprising a linear or branched hydrophobic polyamine backbone having 2 to 10 tertiary amino nitrogen atoms and a spacer between two tertiary nitrogen atoms wherein the spacer is selected from the group consisting of C₈-C₁₆-alkylene, C₅-C₁₅-cycloalkylene,

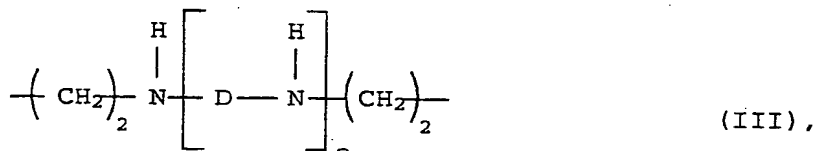
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25

wherein in formulae I, II and III

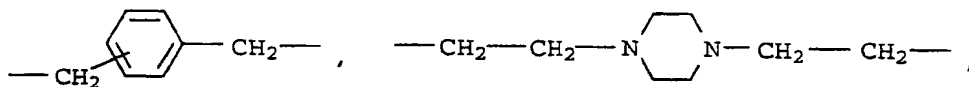
B is C₂-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

D is C₄-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

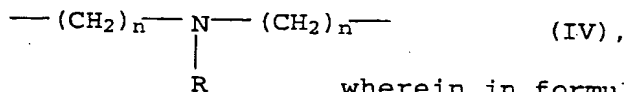
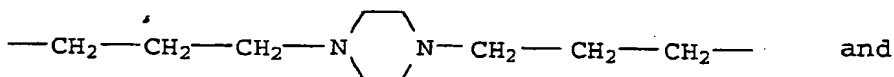
o is 1 or 2,

p is 3 to 8,

30



35



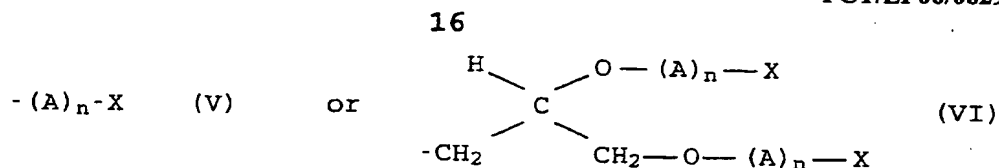
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wherein in formula IV

R = C₁- to C₂₂-alkyl or C₇-C₂₂-aralkyl
and n = 3 to 6,

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at least one tertiary amine end group of the polyamine backbone contains two groups having the formula

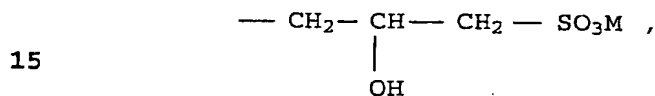


5 wherein

A means an ethylene oxide unit, a propylene oxide unit,
a unit of butylene oxides and a tetrahydrofuran unit,

10 n is a number of from 1 to 50,

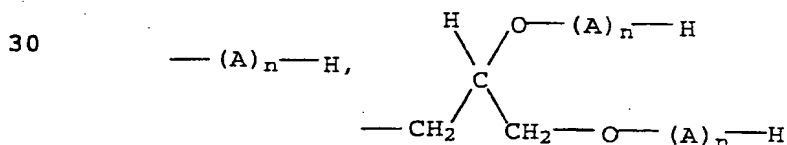
X is — SO₃M , — CH₂— CH₂— SO₃M , — CH₂— CH₂— CH₂— SO₃M ,



with the proviso that in formula VI one X may also be hydro-
gen and

25 M is hydrogen, alkali metal or ammonium,

or contains one group of formula V or VI and one group selec-
ted from radicals consisting of



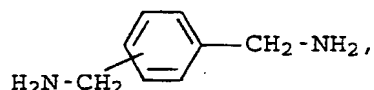
35 C₁- to C₂₂-alkyl and C₇-C₂₂-aralkyl, the meaning of A and n is
the same as in formula V or VI, said zwitterionic polyether-
polyamine having a molecular weight up to 9000 and optionally
containing up to 100% of the nitrogen atoms quaternized.

2. A zwitterionic polyamine as claimed in claim 1, wherein the
40 tertiary nitrogen atoms of the end groups of the polyamine
backbone contain two groups of formula V or VI.

3. A zwitterionic polyamine as claimed in claim 1, wherein the
45 nitrogen atoms of the end groups of the polyamine backbone
are quaternized and contain, as substituents, two groups of

formula V or VI and one C₁- to C₂₂-alkyl group or a hydroxy-alkyl group.

4. A zwitterionic polyamine as claimed in claim 1, wherein the
5 nitrogen atoms of the end groups of the polyamine backbone
are quaternized and contain, as substituents, two groups of
formula V and a C₁- to C₂₂-alkyl group.
5. A zwitterionic polyamine as claimed in claim 1, wherein the
10 nitrogen atoms of the end groups of the polyamine backbone
are quaternized and contain, as substituents, two groups of
formula V and a hydroxyethyl or hydroxypropyl group.
6. A zwitterionic polyamine as claimed in claim 1, wherein the
15 spacer of the polyamine backbone is a cyclic C₅-C₁₅-alkylene
group.
7. A zwitterionic polyamine as claimed in claim 1, wherein the
20 polyamine backbone is derived from a polyamine selected from
the group consisting of bis(hexamethylene)triamine, N,N'-
bis(3-aminopropyl)piperazine, and N,N'-bis(2-amino-
ethyl)piperazine and



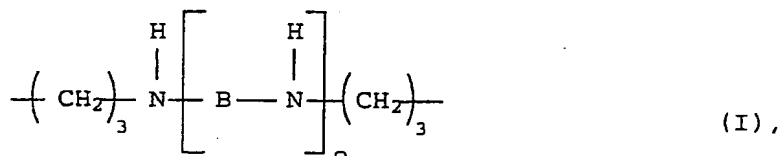
and wherein at least one tertiary amine end group of the
polyamine backbone contains two groups having formula V or
VI.

8. A process for the production of a zwitterionic polyamine
which comprises a first step wherein
- (i) a linear or branched hydrophobic polyamine having 2 to 10
35 primary or secondary amino nitrogen atoms and one spacer
between two nitrogen atoms wherein the spacer is selected
from the group consisting of C₈- to C₁₅-alkylene, C₅- to
C₁₅-cycloalkylene,

40

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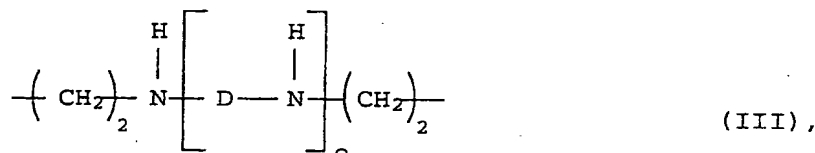
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wherein in formulae I, II and III

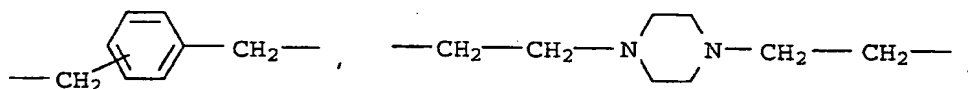
B is C₂-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

D is C₄-C₁₆-alkylene, C₅-C₁₅-cycloalkylene

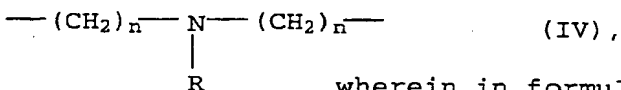
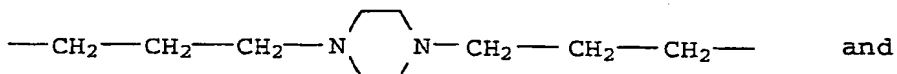
20 o is 1 or 2

p is 3 to 8

25



30



wherein in formula IV

R = C₁- to C₂₂-alkyl or C₇-C₂₂-aralkyl
and n = 3 to 6,

35

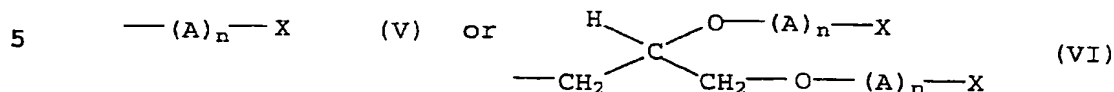
is reacted with

(ii) at least one C₂- to C₄-alkylene oxide or tetrahydrofuran
at such a ratio that on each NH group of the polyamine 1
to 50 units of the alkylene oxide are added,

40

a second step wherein the alkoxyated polyamine obtained in
the first step is reacted with a compound selected from the
group consisting of a halogen sulfonic acid, halogen phospho-
rous acid, vinyl sulfonic acid, propane sultone, halogen ace-
tic acid, acrylic acid, methacrylic acid, vinyl phosphorous
45 acid and the alkali metal or ammonium salts of the said

acids, in such a manner that at least one tertiary amine end group of the alkoxyated polyamine contains two groups having the formula

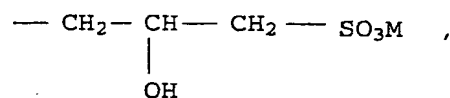


wherein

10 A means an ethylene oxide unit, a propylene oxide unit, a unit of butylene oxides and a tetrahydrofuran unit,

n is a number of from 1 to 50,

15 X is $\text{---SO}_3\text{M}$, $\text{---CH}_2\text{---CH}_2\text{---SO}_3\text{M}$, $\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---SO}_3\text{M}$,

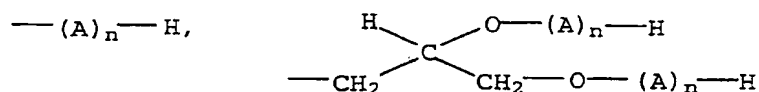


20 $\text{---CH}_2\text{---COOM}$, $\text{---CH}_2\text{---CH}_2\text{---COOM}$,
 $\text{---PO}_3\text{M}$, $\text{---CH}_2\text{---CH}_2\text{---PO}_3\text{M}_2$,

25 with the proviso that in formula VI one X may also be hydrogen and

M is hydrogen, alkali metal or ammonium,

30 or contains one group of formula V or VI and one group selected from radicals consisting of



35 the meaning of A and n is the same as in formula V or VI,
 and optionally

40 a third step wherein up to 100% of the tertiary nitrogen atoms of the reaction product obtained in the second step are quaternized, said degree of quaternization may also be obtained by first quaternizing the reaction product obtained in the first step and subsequently carrying out the second
 45 step.

9. A process is claimed in claim 8, wherein
in the first step

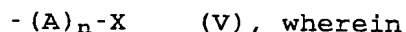
5 (i) a polyamine selected from the group, consisting of
bis(hexamethylene)triamine, bis(aminopropyl)piperazine,
N,N'-bis(aminopropyl)hexamethylenediamine and
N,N,N',N'',N''-penta(2,3-dihydroxypropyl)-bis(hexamethy-
lene)triamine, is reacted with

10 (ii) an alkylene oxide selected from the group consisting of
ethylene oxide, propylene oxide, butylene oxide and mix-
tures of the said alkylene oxides, at such a ratio that
on each NH group of the polyamine 15 to 40 units of the
alkylene oxide are added,

15

in the second step

the alkoxyated polyamine obtained in the first step is
reacted with chlorosulfonic acid in such ratio that at least
one tertiary end group of the polyamine contains two groups
20 having the formula



25 A is an ethylene oxide unit, a propylene oxide unit or a
butylene oxide unit,

n is 15 - 40 and

X is SO₃H,

and

30

in the third step

the zwitterionic reaction product of the second step is quat-
ernized with dimethyl sulfate, methyl chloride or benzyl
chloride.

- 35 10. A process as claimed in claim 8, wherein the alkoxyated
polyamine obtained in the first step is quaternized up to
100 % and subsequently reacted with chlorosulfonic acid.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06296

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G73/02 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 049 680 A (O'LENICK JR ANTHONY J) 17 September 1991 (1991-09-17) claims 1-17	1-10
A	WO 97 28207 A (PROCTER & GAMBLE) 7 August 1997 (1997-08-07) claims 1-8	1-10
A	DE 196 47 060 A (HUELS CHEMISCHE WERKE AG) 20 May 1998 (1998-05-20) claims 1-13	1-10
A	US 4 739 094 A (MAZANEK JAN ET AL) 19 April 1988 (1988-04-19) cited in the application claims 1-11	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

2 November 2000

Date of mailing of the international search report

13/11/2000

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Fax: (+31-70) 340-3016

Authorized officer

Glanddier, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06296

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5049680	A	17-09-1991	NONE	
WO 9728207	A	07-08-1997	US 5747440 A AU 1296397 A AU 2245897 A CA 2230320 A EP 0839160 A US 5929010 A WO 9728208 A	05-05-1998 22-08-1997 22-08-1997 07-08-1997 06-05-1998 27-07-1999 07-08-1997
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